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VIII.

ON A NEW MODE OF MANIPULATING HYDRIC SULPHIDE.

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IN chemical laboratories, where instruction in qualitative analysis is given to large numbers on the class system, the use of hydric sulphide gas as a reagent is attended with grave inconveniences. These evils can in great measure be avoided by substituting for the gas a solution of the reagent in water, saturated at the ordinary temperature and pressure of the air; when, as is well known, one volume of water dissolves about 3.4 volumes of the gas (measured at 15° C. and 76 cm.). Such a solution was for a long time used in the laboratory of Harvard College. It was prepared in a long series of two *litre* bottles connected by glass tubes in the usual way, and the solution was kept in the laboratory in a large tubulated glass flask, from which it was drawn by the students, as occasion required. This solution answers almost every purpose for which the reagent is used in the ordinary course of qualitative analysis, and the few conditions under which it does not give satisfactory results can be easily avoided. Moreover, in ease of application and promptness of effect it has all the advantages of a liquid reagent; and the only inconvenience its use involves is an occasional evaporation of a solution, which the dilution by the reagent may render necessary. Of course a solution of hydric sulphide is liable to oxidation, and soon becomes turbid in contact with the air; but this change can be easily avoided by fitting to the neck of the flask (in which the solution is kept), by means of a rubber stopper, a glass tube dipping under the liquid, and connecting this tube with one of the vents of illuminating gas in the laboratory.

For quantitative work, and for the preparation of chemical products, when considerable quantities of metallic sulphides must be precipitated, a solution of hydric sulphide, saturated under the ordinary pressure of the air, is inconveniently dilute; and two years since we described a simple method by which a solution concentrated under pressure could easily be prepared with the ordinary laboratory appliances. A heavy glass bottle of about four litres' capacity served as a generator, and from this the gas passed through a wash-bottle into two other bottles of the same size and strength as the first. The intermediate bottle was three-fourths filled with water, while the last served simply as a gasholder. The connections were so arranged that the gas, after bubbling up through the water, was delivered at the top of the gasholder; and, by a tube uniting the bottom of the gasholder with the water-pipes of the laboratory, the interior of the apparatus could be submitted to the pressure of a column of water sixty feet high. The gasholder was also provided with an exit tube, which could be closed by a compression cock. The connecting tubes all passed through rubber stoppers which were firmly wired to the necks of the bottles, and the water-bottle was connected with its neighbors by two lengths of stout rubber hose so that the water could be shaken up with the gas without disturbing the rest of the apparatus. In order to saturate the water with hydric sulphide, a charge of ferrous sulphide sulphuric acid and water sufficient to yield at least three times the amount of gas theoretically required was placed in the generator, and, after the connections were made, the gas was allowed to stream through the apparatus until all the air was displaced. The exit tube of the last bottle was then closed, the water pressure turned on and the water-bottle frequently shaken, until absorption ceased, and the aqueduct water — at first forced by its pressure into the gasholder — was driven back into the pipes. Before dismounting the apparatus, the rubber connectors were all closed by compression cocks, and care was taken to vent the generator gradually. Moreover, the connectors of the water-bottle were so arranged that when the apparatus was dismounted a short piece of rubber hose was left attached to each orifice of the bottle, both of which were closed by compression cocks. To one of these a vent tube was subsequently attached, and by this the solution was drawn off at pleasure, as from a soda-water siphon.

This simple apparatus was constantly used by us for two years, and served an excellent purpose; but it was found that after the glass generators had been charged several times they were liable to burst under the same pressure which at first they had readily sustained. The same accident never happened to the other bottles. But of course, if the pressure is long continued, bottles of glass of the size named, however well made, would be liable to such an accident; and, if the apparatus is to be remounted, it would be better to use a metallic vessel for the generator, and to cover the glass bottles with some kind of netting. The experience with the glass apparatus led us to seek to adapt to the same purpose some one of the various soda-water apparatuses which are greatly used in the United States for the production of effervescing drinks. After examining several of the patterns in the market, we selected for trial the one represented below, which is manufactured by the firm of John Matthews, of New York, at their establishment, — First Avenue, 26th and 27th Streets, — in that city. The apparatus was designed by them for preparing that overcharged aqueous solution of carbonic dioxide, which in the United States is familiarly called soda-water; but with a very slight modification it can be used with equal efficiency for the preparation of a similar solution of hydric sulphide. We have worked out the details of the process, which this new application involves, and publish them with the hope that the apparatus may be found of as great value in other laboratories

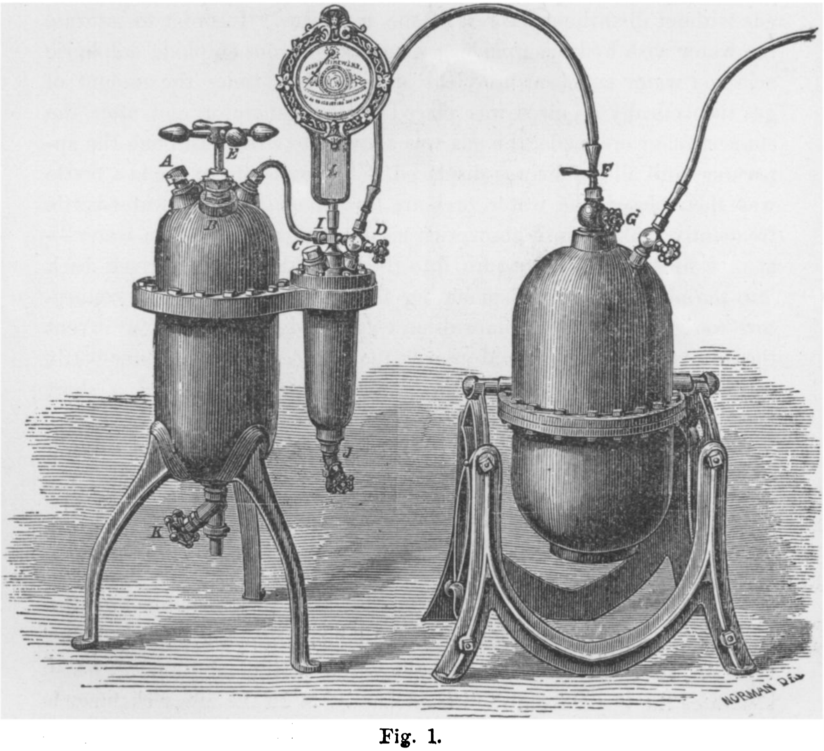

Fig. 1.

as in our own. The wood-cuts are taken from the catalogue of the firm, who have kindly loaned the blocks for this paper; and we would here express our obligations to them for their great courtesy and liberality during the whole course of our experiments.

The apparatus consists of two parts, the generator and the fountains; and in Fig. 1 the generator is represented connected by a rubber hose with one of the fountains, of which in practice we use three, connected in a line by similar lengths of rubber hose, like so many Woolf's bottles. In the figure, only the first of the line is represented, which is set on trunnions in a frame, in order to facilitate the agitation of the water and the gas. Only one of these frames, however, is required, to which the other fountains can readily be transferred. A section of the generator is represented in Fig. 2. It is made of cast iron, and in two parts (readily distinguished in the figure), which are firmly bolted together, so as to confine in its place the bell-metal plate M, which separates the upper from the lower chamber. In the lower chamber is placed dilute sulphuric acid, which is poured in through the bung A.

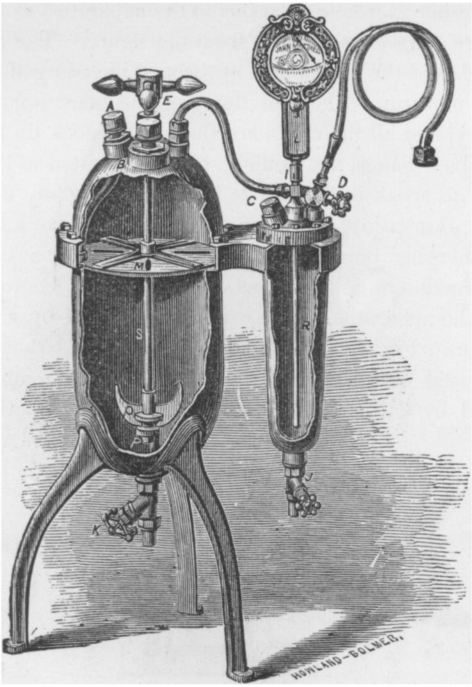

Fig. 2.

In the upper chamber, and resting on the plate, is placed coarsely powdered sulphide of iron, which is put in through the bung B. Through the plate M, and on two lines at right angles to each other, there are cut radial slits, ½ an inch wide, which are guarded by four iron arms. These arms are attached to the agitator shaft S, and move over the surface of the plate, alternately covering and uncovering the slits, when the handle E is turned. To the lower end of the same shaft is fastened the agitator O, which is turned simultaneously with the arms just mentioned. After the apparatus has been charged, it is evident that by turning the handle the sulphide of iron may be sifted down at pleasure into the acid water below; and the handles and arms are so disposed that when the bungs are uncovered by the handles the slits are covered by the arms. From the generator, the gas passes through the washer R, whose relations to the apparatus, as well as that of the pressure gauge, are evident from the figure. The generator is lined with lead, and the rest of the apparatus, including the bell-metal plate M, with pure tin. The lead lining of the generator is seamless and very heavy, and all the cocks are lined with block tin tubing. Of the various valves, bungs, and stuffing boxes indicated in the figure, it is unnecessary to speak in detail. It is sufficient to say that they are of excellent workmanship, and during a year's trial have kept perfectly tight. The charging bung, B, however, is closed by a safety cap of peculiar construction, which deserves special mention, because it insures the safety of the apparatus. The cap is represented by Fig. 3, and a section is given in Fig. 4. It will be seen by the last that the escape of the compressed gas from the generator through the apertures *d* is only prevented by a thin disk *a*, which is shown in detail by Fig. 5.

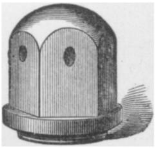
Fig. 3.

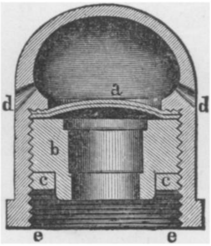

Fig. 4.

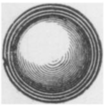
Fig. 5.

This disk is made of two thin plates: the lower one, which comes in contact with the acid spray, is of lead, and the upper one of silvered copper, whose thickness is so adjusted that it must be at once ruptured if the pressure in the apparatus should become unduly great.

Although the so-called soda-water fountains — in which the solution of the gas and water is made — have all in general the same simple relation of parts, they are constructed of very different materials and after very different methods. The outside shell may be either of hammered copper or of some form of iron, and this may be lined with tin, enamel, or glass. After having determined by experiment that a solution of hydric sulphide — especially when some carbonic dioxide is added — exerts no action on a surface of metallic tin, except a very slight and superficial staining, we selected as best adapted to our purpose the steel fountains, also manufactured by the firm of John Matthews, Fig. 6. These are made of plates of steel, united in a peculiar way invented by themselves so as to secure with comparative lightness very great strength. They are lined on the inside with sheet tin, and the tin lining forms an independent vessel, which alone is connected with the bungs. The tubes and valve cocks are also either made or lined with tin, so that the solution never comes in contact with any other metal. For making ordinary soda-water, the fountain requires only a single valve, which connects with a tube leading to the bottom of the vessel, and this serves both to charge the fountain and to draw

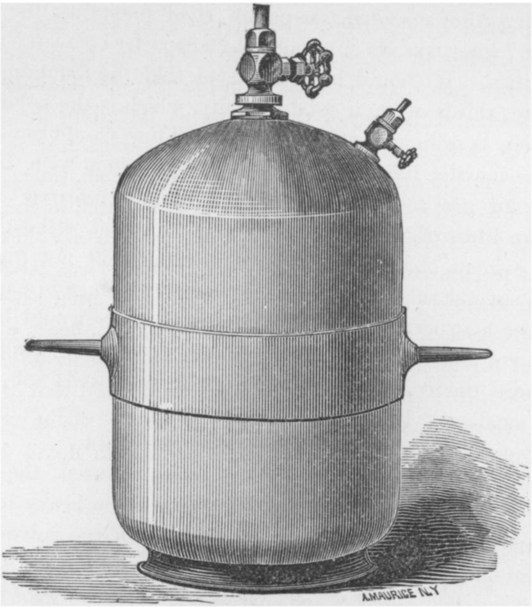

Fig. 6.

off the solution when made. But since a solution of hydric sulphide is rendered turbid if left in contact with even a small quantity of air, and since a variable amount of free hydrogen is always formed by the action of sulphuric acid on common sulphide of iron, it was necessary for our purpose to add to the ordinary fountain a vent cock as shown in the last figure. This enables us to connect together several fountains after the manner of Woolf's bottles as already described, and, by passing the current of gas through the whole line, to drive out all the air originally in the apparatus, as well as the free hydrogen subsequently evolved. Moreover, in the preparation of the solution of hydric sulphide, the generator should be much larger relatively to the fountains than in the preparation of soda-water. Thus we use for charging the so-called six-gallon steel fountains, the "Upright Generator" known as No. 40, which has a capacity below the diaphragm of sixty litres. It should be here stated that the fountains are only rated at two thirds of their total capacity, which is the volume of soda water which is ordinarily made in them. They should never be more than three-fourths filled with water. But, even with this liberal allowance for gas room, the six-gallon fountains referred to will hold twenty-five litres of water. It may also be stated, although the fact must be evident, that a single large fountain will not give as good results as several small ones of equal capacity; since in expelling the air and free hydrogen, as we have described, there would be a considerable loss of material, if only one fountain were used. Still, in laboratories where the consumption is not great, the loss is not important; and the smallest "Upright Generator," with one six-gallon fountain, will be found to be a perfectly satisfactory apparatus.

Assuming first that the larger apparatus is used, the method of charging is as follows: The large generator is too heavy to be readily moved, and should be placed so that the discharge valve will empty directly into a drain. Water also should be brought to the apparatus by hose, — if possible, both hot and cold water, — not only for convenience in charging, but also in washing. Finally, there ought to be a good flue in the neighborhood, into which the waste gas may be discharged. The apparatus having been thus established, the three fountains — first rinsed out — are filled each with twenty-five litres of distilled water, and, the valves having been secured, the fountains are connected with each other and the generator by means of stout rubber hose as already indicated, and the vent valve of the last fountain is connected with the flue by a length of common gas hose. The generator is then charged as follows: The handle is first placed so as to uncover the bungs and cover the slits in the diaphragm. Through the bung A is now poured 40 litres of *hot* water, heated to between 70° and 80° C., and then 5 litres of common oil of vitriol are poured very cautiously into the same bung through a lead funnel with narrow spout provided for the purpose. The acid water will thus be heated nearly to the boiling point, and its capacity of dissolving ferrous sulphate raised to the maximum. Next 6 kilogrammes of sulphide of iron — previously sufficiently pulverized to pass through a wire sieve with eight meshes to the inch, and mixed with two kilogrammes of marble powder — is run through a wide-mouth funnel into the bung B. The bungs having been now all closed, the joints of the apparatus tested, the exit valve D of the generator and all the valves of the fountains opened, a small amount of the powder is sifted down into the acid water by turning the handle not more than a single revolution, always taking care to leave it so that the slits of the diaphragm shall be left covered. The gas is then allowed to stream through the apparatus, and tested as it escapes into the flue, until it burns without explosion, using a small pneumatic trough for that purpose. The air is now nearly expelled, and the escape of gas should be reduced by the last vent valve until the current only supplies a small jet, which may now be attached and lighted with safety, and by the size of this flame the vent may afterwards be regulated. The handles are now slowly turned, and the pressure in the apparatus carried up to about 120 pounds. The valves of the fountains and the valve D of the generator are now all closed, and the two last fountains detached, leaving the first (which is mounted on a frame as represented in Fig. 1) united to the generator as before. This is now rocked for several minutes to and fro, in order to thoroughly agitate the water with the gas. The stop valve G should then be opened, and then the valve D (very gradually), so that the gas may be admitted slowly to the fountain. The valves are then again closed, and the agitation renewed, and the same operation is repeated several times until no more gas is absorbed by the water in the fountain, the pressure in the generator meanwhile being maintained at 120 lbs., by turning the handle. The first fountain is then removed, and the same process repeated with each of the others. At the close of the operation, after all chemical action has ceased, there remains in the generator — both free and dissolved in the liquid residue — a large volume of hydric sulphide gas. This we economize by venting the generator slowly through Woolf's bottles containing aqua ammonia, and thus preparing at the same time ammonic sulphide. It is not unimportant to add that the generator should be emptied before it cools, and the ferrous sulphate has time to crystallize. The discharge valve R should then be removed, and the whole apparatus thoroughly washed out. If the valve becomes clogged, it can generally be cleared by developing pressure in the generator by means of a small charge of ground marble. Otherwise, after the pressure has been relieved, and the upper valves and bungs closed, the discharge valve must be cautiously removed, and an opening forced through the lower bung. Such details are necessary in order that others may profit by our experience; but, lest the details should convey the impression that the apparatus is complicated, and that the process requires skilled labor, it may be stated that in this laboratory the apparatus is entirely in charge of a laboratory servant, and may be managed by any workman of ordinary intelligence. It does not require more than four hours to work over a single charge, and this yields 75 litres of hydric sulphide solution under a pressure of 120 lbs. According to our experience, this supply lasts with a class of one hundred students in qualitative analysis about a month. For laboratories where the classes are much smaller than this, we should recommend the smallest size generator, which may be used with a single six-gallon fountain. The smaller apparatus is managed in precisely the same way as the larger, only taking one half the quantity of materials. It is important as before to wash out in the first place all the air, and to maintain a small current of gas through the vent valve of the fountain while the pressure in the apparatus is rising. This of course entails some loss of hydric sulphide; but the chief loss is caused by the venting of the generator, and all this gas may be utilized for the preparation of alkaline sulphides as described above, or this waste gas may be used for washing out the air from a second fountain, and thus preparing it for a subsequent charge.

For dispensing the reagent in our *qualitative* laboratory, we place the fountain in a cupboard and connect it by a block-tin tube with a so called "draught column," Fig. 7, in the ventilating hood above. From this each student draws the reagent as it is required. In quantitative work we may draw the charged water directly from the fountain into the midst of the solution to be treated, using simply a common rubber hose terminated by a glass tube which dips under the surface of the liquid: the hose is attached to the nipple of a cap which screws on to the valve of the fountain, and by confining two or more disks of linen cloth between the cap and the head of the valve (like washers) we can filter the solution as it flows out. It is more convenient, however, to distribute the reagent to advanced students in the well-known soda-water siphon, Fig. 8. These require no description, but as the simple apparatus used for filling the siphon is not yet a familiar object in chemical laboratories, we give a figure of the apparatus (Fig. 9), taken, like our other cuts, from the catalogue of John Matthews. By pressing the foot on a pedal shown at the base of the apparatus, the siphon — confined in a cage — is raised, so that its mouth is forced tightly against one opening of a valve of peculiar construction, the second opening of which is united by a block-tin tube to a fountain; while at the same time the handle of the siphon is pressed back. On now pushing the upper lever shown in the cut to the right, the valve of the fountain having been previously opened, a connection is made between the fountain and the siphon; when the charged water rushes into the latter, condensing the air to a fraction of its original volume. If next the same lever is pushed momentarily to the left, the first connection is closed; while a vent is opened, through which the condensed air rushes out into the atmosphere before the gas in solution has time to escape, and then on pushing back the handle a further portion of liquid enters, nearly filling the interior of the bottle. Lastly, on raising the foot, the valve of the siphon shuts at the same time that the bottle is lowered and released from its cage, — the whole process being the work of a few seconds. At the first filling, there sometimes remains a small amount of air in the siphon, so that the solution becomes slightly turbid on standing; but this effect of oxidation can be easily avoided by using a sufficient amount of marble powder

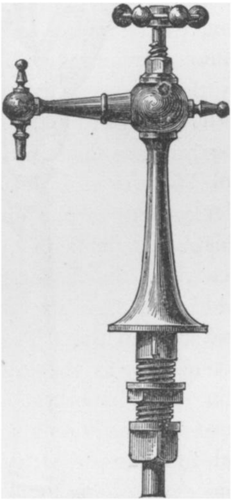

Fig. 7.

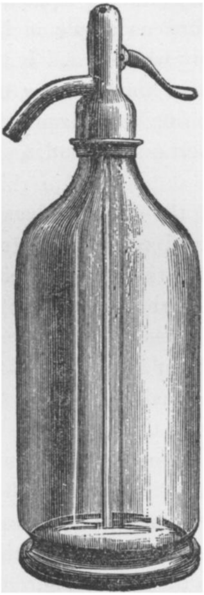

Fig. 8.

in charging the generator. This siphon unquestionably affords the most convenient mode of using hydric sulphide; and for a private laboratory a single siphon, well charged, will afford as ample a supply as will ordinarily be needed. It is greatly to be hoped that our manufacturing chemists may soon find an advantage in supplying this important reagent in such an elegant form.*

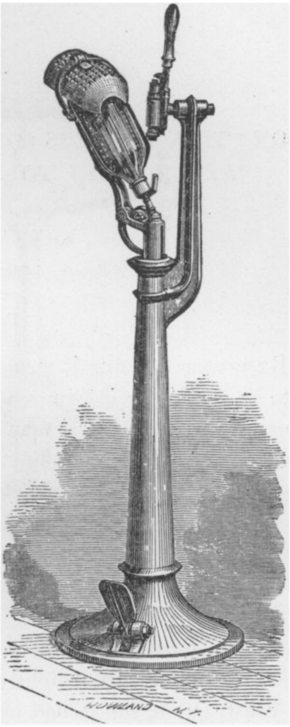

Fig. 9.

When the water is charged as directed above, it of course holds in solution, besides hydric sulphide, a considerable volume of carbonic dioxide; and if, under any circumstance, the presence of this last gas would produce an injurious effect, the marble powder can be simply omitted in charging the generator. In almost all cases, however, the carbonic dioxide exerts a very beneficial influence, and in several ways. In the first place, it insures the non-action of the hydric sulphide on the metallic surfaces of the apparatus. In the second place, it protects the solution from the action of the air when it is drawn into an open vessel, so that after a metallic sulphide has been precipitated by an excess of the reagent, the products may be digested in an open flask or beaker without fear of oxidation. In the third place, the carbonic dioxide adds greatly to the tension of the confined gas, and enables us to develop sufficient pressure to charge the siphon without unnecessarily increasing the strength of the solution of hydric sulphide.

CHEMICAL LABORATORY OF HARVARD COLLEGE, 1876.

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* All the apparatus here described may be obtained from the firm of John Matthews, First Avenue, 26th and 27th Streets, New York, at very reasonable rates. Be careful in ordering to state the use to which the apparatus is to be put, with the caution that no silver plating or lead paint should be used upon it.